



(11) **EP 1 672 034 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**25.05.2011 Bulletin 2011/21**

(51) Int Cl.:  
**C09B 67/50** <sup>(2006.01)</sup> **C09B 67/16** <sup>(2006.01)</sup>  
**C09B 67/12** <sup>(2006.01)</sup> **G03G 5/06** <sup>(2006.01)</sup>

(21) Application number: **05110944.5**

(22) Date of filing: **18.11.2005**

(54) **Processes for the preparation of high sensitivity titanium phthalocyanines photogenerating pigments**

Verfahren zur Herstellung von bilderzeugenden hochsensiblenTitanylphthalocyaninpigmenten

Procédé pour la préparation de pigments du type titanyl-phthalocyanines à sensibilité élevée formant une image

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **18.11.2004 US 992500**

(43) Date of publication of application:  
**21.06.2006 Bulletin 2006/25**

(73) Proprietor: **Xerox Corporation**  
**Rochester,**  
**New York 14644 (US)**

(72) Inventors:  
• **Wu, Jin**  
**Webster, NY 14580 (US)**  
• **Lin, Liang-Bih**  
**Rochester, NY 14618 (US)**  
• **Hor, Ah-Mee**  
**Mississauga, Ontario L5L 5B1 (CA)**

• **Gaynor, Roger E.**  
**Oakville, Ontario L6L 5G7 (CA)**  
• **Galloway, Justin F.**  
**Webster, NY 14580 (US)**

(74) Representative: **Grünecker, Kinkeldey,**  
**Stockmair & Schwanhäusser**  
**Anwaltssozietät**  
**Leopoldstrasse 4**  
**80802 München (DE)**

(56) References cited:  
**EP-A- 0 409 737 EP-A- 0 460 565**  
**EP-A- 0 482 922 EP-A- 0 508 772**  
**EP-A- 0 516 433 EP-A- 0 560 311**  
**EP-A- 0 810 267 EP-A- 1 093 025**  
**WO-A-99/45074 US-A- 5 153 094**  
**US-A- 5 189 155 US-A- 5 189 156**  
**US-A- 5 288 574 US-A- 5 334 478**  
**US-A- 5 350 844 US-A- 5 473 064**

**EP 1 672 034 B1**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description**

5 [0001] Illustrated herein, in various exemplary embodiments, are processes for preparing high sensitivity titanyl phthalocyanine pigments. The phthalocyanine pigments prepared by the processes disclosure are suitable for use as a photo-generating pigment in a photoimaging device and will be described with particular reference thereto.

10 [0002] In the art of electrophotography, an electrophotographic plate comprising a photoconductive insulating layer on a conductive layer is imaged by first uniformly electrostatically charging the imaging surface of the photoconductive insulating layer. The plate is then exposed to a pattern of activating electromagnetic radiation such as light, which selectively dissipates the charge in the illuminated areas of the photoconductive insulating layer while leaving behind an electrostatic latent image in the non-illuminated area. This electrostatic latent image may then be developed to form a visible image by depositing finely divided electroscopic toner particles on the surface of the photoconductive insulating layer. The resulting visible toner image can be transferred to a suitable receiving member such as paper. This imaging process may be repeated many times with reusable electrophotographic imaging members.

15 [0003] The electrophotographic imaging members may be in the form of plates, drums or flexible belts. These electrophotographic members are usually multilayered photoreceptors that comprise a substrate, a conductive layer, an optional hole blocking layer, an optional adhesive layer, a charge generating layer, a charge transport layer, an optional overcoating layer and, in some belt embodiments, an anticurl backing layer. One type of multilayered photoreceptor comprises a layer of finely divided particles of a photoconductive inorganic compound dispersed in an electrically insulating organic resin binder. In U.S. Pat. No. 4,265,990 a layered photoreceptor is disclosed having separate charge generating (photogenerating) sections and charge transport layers. The charge generation section is capable of photogenerating holes and injecting the photogenerated holes into the charge transport layer.

20 [0004] The charge generating section utilized in multilayered photoreceptors include, for example, inorganic photoconductive particles or organic photoconductive particles dispersed in a film forming polymeric binder. Inorganic or organic photoconductive material may be formed as a continuous, homogeneous charge generation section. Many suitable photogenerating materials known in the art may be utilized, if desired.

25 [0005] Electrophotographic imaging members or photoreceptors having varying and unique properties are needed to satisfy the vast demands of the xerographic industry. The use of organic photogenerating pigments such as perylenes, bisazos, perinones, and polycyclic quinones in electrophotographic applications is well known. Generally, layered imaging members with the aforementioned pigments exhibit acceptable photosensitivity in the visible region of the light spectrum, and hence they are particularly suitable for use in electrophotographic processes where visible light sources such as tungsten, fluorescent, and xenon lamps are used.

30 [0006] However, these classes of pigments in many instances have low or negligible photosensitivity in the near infrared region of the spectrum, for example between 750 and 970 nanometers, thereby preventing their selection for photoresponsive imaging members in electronic printers wherein electronic light emitting devices, such as GaAs diode lasers, are commonly used as a light source to create an electrostatic image on the imaging members. Also, some of the above mentioned organic pigments have a narrow and restricted spectral response range such that they cannot reproduce certain colors present in the original documents, thus resulting in inferior copy quality.

35 [0007] To satisfy these demands, photoreceptors with different charge generation section formulations providing varying photosensitivities may be utilized. Charge generation sections are often formed by layering a dispersion of photoconductive pigments on to the photoreceptor. The cost to develop different photoconductive pigments and different charge generation section coating dispersion formulations and to change dispersion solutions for different products in the manufacturing process greatly increases the costs to manufacture photoreceptors.

40 [0008] The process of making a photoreceptor using dispersions is strongly susceptible to many variables, such as, for example, materials variables, including contents and purity of the material; process variables, including milling time and milling procedure; and coating process variables, including web coating, dip coating, the drying process of several layers, the time interval between the coatings of successive layers etc. The net outcome of all these variables is that the electrical characteristics of photoreceptors may be inconsistent during the manufacturing process.

45 [0009] Sensitivity is a very important electrical characteristic of electrophotographic imaging members or photoreceptors. Sensitivity may be described in two aspects. The first aspect of sensitivity is spectral sensitivity, which refers to sensitivity as a function of wavelength. An increase in spectral sensitivity implies an appearance of sensitivity at a wavelength in which previously no sensitivity was detected. The second aspect of sensitivity, broadband sensitivity, is a change of sensitivity (e.g., an increase) at a particular wavelength previously exhibiting sensitivity, or a general increase of sensitivity encompassing all wavelengths previously exhibiting sensitivity. This second aspect of sensitivity may also be described as change of sensitivity, encompassing all wavelengths, with a broadband (white) light exposure. A common problem encountered in the manufacturing of photoreceptors is maintaining consistent spectral and broadband sensitivity from batch to batch.

50 [0010] Typically, flexible photoreceptor belts are fabricated by depositing the various layers of photoactive coatings onto long webs that are thereafter cut into sheets. The opposite ends of each photoreceptor sheet are overlapped and

ultrasonically welded together to form an imaging belt. In order to increase throughput during the web coating operation, the webs to be coated have a width of twice the width of a final belt. After coating, the web is slit lengthwise and thereafter transversely cut into predetermined lengths to form photoreceptor sheets of precise dimensions that are eventually welded into belts. The web length in a coating run may be many thousands of feet long and the coating run may take more than an hour for each layer.

**[0011]** Of particular interests are titanil phthalocyanines. Titanil phthalocyanines, or oxytitanium phthalocyanines, are suitable photogenerating pigments known to absorb near infrared light around 800 nanometers and have generally exhibited improved sensitivity compared to other pigments such as, for example, hydroxygallium phthalocyanine. Titanil phthalocyanine is known to exhibit certain crystal phases or polymorphs. Generally, titanil phthalocyanine is known to have five main crystal forms known as Types I, II, III, X, and IV. The various polymorphs of titanil phthalocyanine have been demonstrated as suitable pigments in the charge or photogenerating layer of a photoimaging member or device. Various methods for preparing a titanil phthalocyanine having a particular crystal phase have been demonstrated. For example, U. S. Patent Nos. 5,189,155 and 5,189,156 discuss a number of prior methods for obtaining various polymorphs of titanil phthalocyanine. Additionally, U.S. Patent Nos. 5,189,155 and 5,189,156 are directed to processes for obtaining Type I, X, and IV phthalocyanines. U.S. Patent No. 5,153,094 relates to the preparation of titanil phthalocyanine polymorphs including Type I, II, III, and IV polymorphs. U.S. Patent No. 5,166,339 discloses processes for preparing Type I, IV, and X titanil phthalocyanine polymorphs, as well as the preparation of two polymorphs designated as Type Z-1 and Type Z-2.

**[0012]** To obtain a titanil phthalocyanine-based photoreceptor having high sensitivity to near infrared light, it is believed necessary to control not only the purity and chemical structure of the pigment, as is generally the situation with organic photoconductors, but also to prepare the pigment in the correct crystal modification. Consequently, it is still desirable to provide a process for preparing titanil phthalocyanines that will provide high sensitivity titanil phthalocyanines.

**[0013]** WO-A-99/45074 discloses a crystalline titanil phthalocyanine showing an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $9.0^\circ$ ,  $9.5^\circ$ ,  $14.3^\circ$ ,  $24.1^\circ$ , and  $27.3^\circ$ . This publication further discloses a photoconductive member comprising a substrate, a charge generating layer containing said titanil phthalocyanine, and a charge transport layer.

**[0014]** EP-A-0482922 discloses a crystalline oxytitanium phthalocyanine showing an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $9.0^\circ$ ,  $14.2^\circ$ ,  $23.9^\circ$ , and  $27.1^\circ$ . An electrophotographic photosensitive member comprising a substrate, a charge generating layer containing said oxytitanium phthalocyanine, and a charge transport layer is also disclosed in this publication.

**[0015]** EP-A-0409737 discloses a crystalline oxytitanium phthalocyanine showing an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $9.0^\circ$ ,  $14.2^\circ$ ,  $23.9^\circ$ , and  $27.1^\circ$ . This publication further discloses an electrophotosensitive member comprising a support having provided thereon a photosensitive layer containing said oxytitanium phthalocyanine. The photosensitive layer may be a laminate structure comprising a charge generating layer, and a charge transport layer. In the laminate structure, the oxytitanium phthalocyanine is contained in the charge generating layer.

**[0016]** EP-A-0810267 discloses a crystalline oxytitanium phthalocyanine showing an x-ray diffraction pattern having strong diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $9.6^\circ$ ,  $24.2^\circ$ , and  $27.3^\circ$ , and weak and broad peaks at about  $11.6^\circ$ ,  $13.5^\circ$ ,  $14.3^\circ$ , and  $18.1^\circ$ . A photoreceptor for electrophotography comprising a support, a charge generating layer containing said oxytitanium phthalocyanine, and a charge transport layer is also disclosed in this publication.

**[0017]** An electrophotographic photoreceptor containing a titanil phthalocyanine showing an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $24.1^\circ$ , and  $27.2^\circ$  is also known from EP-A-0560311.

**[0018]** The present invention provides a process for the preparation of a Type V titanil phthalocyanine having an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $9.0^\circ$ ,  $9.6^\circ$ ,  $24.0^\circ$ , and  $27.2^\circ$ , the process comprising the steps of providing a Type I titanil phthalocyanine; dissolving said Type I titanil phthalocyanine in a solution comprising a trihaloacetic acid and an alkylene halide; adding said mixture comprising the dissolved Type I titanil phthalocyanine to a solution comprising an alcohol and an alkylene halide thereby precipitating a Type Y titanil phthalocyanine; and treating said Type Y titanil phthalocyanine with monochlorobenzene to yield a Type V titanil phthalocyanine.

**[0019]** The present invention further provides a process for the preparation of Type V titanil phthalocyanine having an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta \pm 0.2^\circ$  at about  $9.0^\circ$ ,  $9.6^\circ$ ,  $24.0^\circ$ , and  $27.2^\circ$ , the process comprising the steps of dissolving a Type I titanil phthalocyanine in a solution of trifluoroacetic acid and methylene chloride; precipitating a Type Y titanil phthalocyanine by adding said solution of trifluoroacetic acid, methylene chloride and the Type I titanil phthalocyanine to a solution of methanol and methylene chloride; washing said Type Y titanil phthalocyanine; and converting the Type Y titanil phthalocyanine to a Type V titanil phthalocyanine by treating said Type Y titanil phthalocyanine with monochlorobenzene.

**[0020]** Preferred embodiments of the present invention are set forth in the subclaims.

FIGURE 1 is a schematic cross-sectional view of a negatively charged photo responsive imaging member comprising a titanyle phthalocyanine;

FIGURE 2 is a schematic cross-sectional view of a positively charged photo responsive imaging member comprising a titanyle phthalocyanine;

FIGURE 3 is a diffractograph summary of an XRPD of a Type Y titanyle phthalocyanine;

FIGURE 4 is a diffractograph summary of an XRPD of a Type V titanyle phthalocyanine;

FIGURE 5 is a diffractograph summary of an XRPD of a Type IV titanyle phthalocyanine of Comparative Example I;

FIGURE 6 is a TEM photograph of a Type V titanyle phthalocyanine prepared according to one embodiment of the present disclosure;

FIGURE 7 is a SEM photograph of a Type V titanyle phthalocyanine prepared according to one embodiment of the present disclosure;

FIGURE 8 is a SEM photograph of a Type IV titanyle phthalocyanine of Comparative Example I; and

FIGURE 9 is a UV spectrum of charge generating dispersions comprising titanyle phthalocyanine pigments.

**[0021]** The present disclosure relates to processes for preparing a high sensitivity titanyle phthalocyanine pigments. The pigments produced by the processes exhibit a crystal phase that is distinguishable from other known titanyle phthalocyanine polymorphs, and are designated as Type V polymorphs. The processes generally comprise converting a Type I titanyle phthalocyanine to a Type V phthalocyanine pigment. The processes include converting a Type I titanyle phthalocyanine to an intermediate phthalocyanine, which is designated as a Type Y phthalocyanine, and then subsequently converting the Type Y phthalocyanine to a Type V titanyle phthalocyanine.

**[0022]** In one embodiment, a process for preparing a high sensitivity titanyle phthalocyanine pigment is illustrated. The process comprises: (a) dissolving a Type I titanyle phthalocyanine in a suitable solvent; (b) adding the solvent solution comprising the dissolved Type I titanyle phthalocyanine to a quenching solvent system to precipitate an intermediate titanyle phthalocyanine (designated as a Type Y titanyle phthalocyanine); and (c) treating the resultant Type Y phthalocyanine with a halo, such as, for example, monochlorobenzene to obtain a resultant high sensitivity titanyle phthalocyanine, which is designated herein as a Type V titanyle phthalocyanine. In another embodiment, prior to treating the Type Y phthalocyanine with a halo, such as monochlorobenzene, the Type Y titanyle phthalocyanine may be washed with various solvents including, for example, water, and/or methanol. The quenching solvents system to which the solution comprising the dissolved Type I titanyle phthalocyanine is added comprises a trihaloacetic acid and an alkylene halide.

**[0023]** The process further provides a titanyle phthalocyanine having a crystal phase distinguishable from other known titanyle phthalocyanines. The titanyle phthalocyanine prepared by a process according to the present disclosure, which is designated as a Type V titanyle phthalocyanine, is distinguishable from, for example, Type IV titanyle phthalocyanines, in that a Type V titanyle phthalocyanine exhibits an x-ray powder diffraction spectrum having four characteristic peaks at 9.0°, 9.6°, 24.0°, and 27.2°, while Type IV titanyle phthalocyanines typically exhibit only three characteristic peaks at 9.6°, 24.0°, and 27.2°.

**[0024]** Any Type I titanyle phthalocyanine may be employed as the starting material in the present process. Type I titanyle phthalocyanines suitable for use in the present process may be obtained by any suitable method. Examples of suitable methods for preparing Type I titanyle phthalocyanines include those disclosed in U.S. Patent Nos. 5,153,094; 5,166,339; 5,189,155; and 5,189,156.

**[0025]** A Type I titanyle phthalocyanine may be prepared, in one embodiment by the reaction of DI<sup>3</sup> (1,3-diiminoisoin-dolene) and tetrabutoxide in the presence of 1-chloronaphthalene solvent, whereby there is obtained a crude Type I titanyle phthalocyanine, which is subsequently purified, up to 99.5 percent purity, by washing with, for example, dimethylformamide.

**[0026]** In another embodiment, for example, a Type I titanyle phthalocyanine can also be prepared by i) the addition of 1 part titanium tetrabutoxide to a stirred solution of from 1 part to 10 parts and, in embodiments, about 4 parts of 1,3-diiminoisoin-dolene; ii) relatively slow application of heat using an appropriate sized heating mantle at a rate of 1 degree per minute to 10 degrees per minute and, in embodiments, about 5 degrees per minute until refluxing occurs at a temperature of from 130 degrees to 180 degrees (all temperatures are in Centigrade unless otherwise indicated); iii) removal and collection of the resulting distillate, which was shown by NMR spectroscopy to be butyl alcohol, in a dropwise fashion, using an appropriate apparatus such as a Claisen Head condenser, until the temperature of the reactants reaches from 190 degrees to 230 degrees and, in embodiments, about 200 degrees; iv) continued stirring at said reflux temperature for a period of 1/2 hour to 8 hours and, in embodiments, about 2 hours; v) cooling of the reactants to a temperature of 130 degrees to 180 degrees, and, in embodiments about 160 degrees, by removal of the heat source; vi) filtration of the flask contents through, for example, an M-porosity (10 to 15 micron) sintered glass funnel which was preheated using a solvent which is capable of raising the temperature of said funnel to about 150 degrees, for example, boiling N,N-dimethylformamide in an amount sufficient to completely cover the bottom of the filter funnel so as to prevent blockage of said funnel; vii) washing the resulting purple solid by slurring said solid in portions of boiling DMF either in the funnel or in a separate vessel in a ratio of 1 to 10, and preferably about 3 times the volume of the solid being washed,

until the hot filtrate became light blue in color; viii) cooling and further washing the solid of impurities by slurring said solid in portions of N,N-dimethylformamide at room temperature, about 25 degrees, approximately equivalent to about three times blue in color; ix) washing the solid of impurities by slurring said solid in portions of an organic solvent, such as methanol, acetone, water and the like, and in this embodiment methanol, at room temperature (about 25 degrees) approximately equivalent to about three times the volume of the solid being washed, until the filtrate became light blue in color; x) oven drying the purple solid in the presence of a vacuum or in air at a temperature of from 25 degrees to 200 degrees, and, in embodiments at about 70 degrees, for a period of from 2 hours to 48 hours and, in embodiments for about 24 hours, thereby resulting in the isolation of a shiny purple solid which was identified as being Type I titanyl phthalocyanine by its X-ray powder diffraction trace.

**[0027]** In still another embodiment, a Type I titanyl phthalocyanine may be prepared by: (i1) reacting a  $DI^3$  with a titanium tetra alkoxide such as, for example, titanium tetrabutoxide at a temperature of about 195°C for about two hours; (ii) filtering the contents of the reaction to obtain a resulting solid; (iii) washing the solid with dimethylformamide (DMF); (iv) washing with four percent ammonium hydroxide; (v) washing with deionized water; (vi) washing with methanol; (vii) reslurrying the washes and filtering; and (viii) drying at about 70°C under vacuum to obtain a Type I titanyl phthalocyanine.

**[0028]** In a process for preparing a high sensitivity phthalocyanine in accordance with the present disclosure, a Type I titanyl phthalocyanine is dissolved in a suitable solvent. In embodiments, a Type I titanyl phthalocyanine is dissolved in a solvent comprising a trihaloacetic acid and an alkylene halide. The alkylene halide comprises, in embodiments, from one to six carbon atoms. Generally, the trihaloacetic acid is not limited in any manner. An example of a suitable trihaloacetic acid includes trifluoroacetic acid. In one embodiment, the solvent for dissolving a Type I titanyl phthalocyanine comprises trifluoroacetic acid and methylene chloride. In embodiments, the trihaloacetic acid is present in an amount of from one volume part to 100 volume parts of the solvent and the alkylene halide is present in an amount of from one volume part to 100 volume parts of the solvent. In one embodiment, the solvent comprises methylene chloride and trifluoroacetic acid in a volume-to-volume ratio of about 4 to 1. The Type I titanyl phthalocyanine is dissolved in the solvent by stirring for an effective period of time such as, for example, for 30 seconds to 24 hours, at room temperature. In one embodiment, the Type I titanyl phthalocyanine is dissolved by stirring in the solvent for about one hour at room temperature (i.e., about 25°C). The Type I titanyl phthalocyanine may be dissolved in the solvent in either air or in an inert atmosphere (e.g., argon or nitrogen).

**[0029]** In a process in accordance with the present disclosure, the Type I titanyl phthalocyanine is converted to an intermediate titanyl phthalocyanine form prior to conversion to the high sensitivity titanyl phthalocyanine pigment. As used herein, "intermediate" does not refer to the life span of the Type Y titanyl phthalocyanine, but rather is used to indicate that the Type Y titanyl phthalocyanine is a separate form prepared in the process prior to obtaining the final desired Type V titanyl phthalocyanine product. To obtain the intermediate form, which is designated as a Type Y titanyl phthalocyanine, the dissolved Type I titanyl phthalocyanine is added to a quenching system comprising an alkyl alcohol and alkylene chloride. Adding the dissolved Type I titanyl phthalocyanine to the quenching system causes the Type Y titanyl phthalocyanine to precipitate. Materials suitable as the alkyl alcohol component of the quenching system include methanol, ethanol, and the like. In embodiments, the alkylene chloride component of the quenching system comprises from one to six carbon atoms. In one embodiment, the quenching system comprises methanol and methylene chloride. The quenching system comprises an alkyl alcohol to alkylene chloride ratio of from 1/4 to 4/1 (v/v). In other embodiments, the ratio of alkyl alcohol to alkylene chloride is from 1/1 to 3/1 (v/v). In one embodiment, the quenching system comprises methanol and methylene chloride in a ratio of about 1/1 (v/v). In another embodiment, the quenching system comprises methanol and methylene chloride in a ratio of about 3/1 (v/v). In embodiments, the dissolved Type I titanyl phthalocyanine is added to the quenching system at a rate of from 1ml/min to 100ml/min, and the quenching system is maintained at a temperature of from 0 to -25°C during quenching. In a further embodiment, the quenching system is maintained at a temperature of from 0 to -25°C for a period of from 0.1 hour to 8 hours after addition of the dissolved Type I titanyl phthalocyanine solution.

**[0030]** Following precipitation of the Type Y titanyl phthalocyanine, the precipitates may be washed with any suitable solution, including, for example, methanol, cold deionized water, hot deionized water, and the like. Generally, washing the precipitate will also be accompanied by filtration. A wet cake containing Type Y titanyl phthalocyanine and water is obtained with water content varying from 30 to 70 weight percent of the wet cake.

**[0031]** A Type V titanyl phthalocyanine is obtained in a process in accordance with the present disclosure by treating the obtained intermediate Type Y titanyl phthalocyanine with a halo, such as, for example, monochlorobenzene. The Type Y titanyl phthalocyanine wet cake may be redispersed in monochlorobenzene, filtered and oven-dried at a temperature of from 60 to 85°C to provide the resultant Type V titanyl phthalocyanine. The monochlorobenzene treatment may occur over a period of one to 24 hours. In one embodiment, the monochlorobenzene is carried out for a period of about five hours.

**[0032]** A titanyl phthalocyanine obtained by a process in accordance with the present disclosure, which is designated as a Type V titanyl phthalocyanine, exhibits an x-ray powder diffraction spectrum distinguishable from other known titanyl phthalocyanine polymorphs. A Type V titanyl phthalocyanine obtained by a process in accordance with the present

disclosure exhibits an x-ray diffraction spectrum having four characteristics peaks at 9.0°, 9.6°, 24.0°, and 27.2°. A titanyl phthalocyanine prepared by a process in accordance with the present disclosure may have a particle size of from 10nm to 500nm. Particle size may be controlled or affected by the quenching rate in adding the dissolved Type I titanyl phthalocyanine to the quenching system and the composition of the quenching system.

5 [0033] Type V titanyl phthalocyanine pigments prepared by a process according to the present disclosure are suitable for use as a photogenerating pigment in the charge generation layer of a photoreceptor for a xerographic or electrostaticographic imaging device. The configuration of the photoimaging device is not limited in any manner and a titanyl phthalocyanine pigment prepared by a process according to the present disclosure may be used in any such device. Examples of suitable photoimaging members include the imaging members depicted in FIGURES 1 and 2.

10 [0034] With reference to FIGURE 1, a negatively charged photoimaging member comprises a supporting substrate 1, a solution coating adhesive layer 2, a photogenerator 3 comprising a Type V titanyl phthalocyanine obtained via a process according to the present disclosure, and a charge transport layer 4.

15 [0035] With reference to FIGURE 2, a positively charged photoimaging member comprises a substrate 10, a charge transport layer 12, and a photogenerator layer 14 comprising a titanyl phthalocyanine obtained via a process according to the present disclosure.

### Preparation of Titanyl Phthalocyanine Compositions

#### **EXAMPLE I: Preparation of Type I Titanyl Phthalocyanine**

20 [0036] A Type I titanyl phthalocyanine was prepared as follows: To a 300 milliliter three-necked flask fitted with mechanical stirrer, condenser and thermometer maintained under an argon atmosphere was added 3.6 grams (0.025 mole) of 1,3-diiminoisoindoline, 9.6 grams (0.075 mole) of o-phthalonitrile, 75 milliliters (80 weight percent) of N-methyl pyrrolidone and 7.11 grams (0.025 mole) of titanium tetrapropoxide (all obtained from Aldrich Chemical Company except phthalonitrile which was obtained from BASF). The resulting mixture (20 weight percent of solids) was stirred and warmed to reflux (about 198°C) for 2 hours. The resultant black suspension was cooled to about 150°C and then was filtered by suction through a 350 milliliter, M-porosity sintered glass funnel, which had been preheated with boiling dimethyl formamide (DMF). The solid Type I TiOPc product resulting was washed with two 150-milliliter portions of boiling DMF and the filtrate, initially black, became a light blue-green color. The solid was slurried in the funnel with 150 milliliters of boiling DMF and the suspension was filtered. The resulting solid was washed in the funnel with 150 milliliters of DMF at 25°C and then with 50 milliliters of methanol. The resultant shiny purple solid was dried at 70°C overnight to yield 10.9 grams (76 percent) of pigment, which was identified as Type I TiOPc on the basis of its X-ray powder diffraction trace. Elemental analysis of the product indicated C, 66.54; H, 2.60; N, 20.31; and Ash (TiO<sub>2</sub>), 13.76. TiOPc requires (theory): C, 66.67; H, 2.80; N, 19.44; and Ash, 13.86.

35 [0037] A Type I titanyl phthalocyanine can also be prepared in 1-chloronaphthalene as follows: A 250 milliliter three-necked flask fitted with mechanical stirrer, condenser and thermometer maintained under an atmosphere of argon was charged with 1,3-diiminoisoindolene (14.5 grams), titanium tetrabutoxide (8.5 grams) and 75 milliliters of 1-chloronaphthalene (CINp). The mixture was stirred and warmed. At 140°C the mixture turned dark green and began to reflux. At this time the vapor (which was identified as n-butanol by gas chromatography) was allowed to escape to the atmosphere until the reflux temperature reached 200°C. The reaction was maintained at this temperature for two hours then was cooled to 150°C. The product was filtered through a 150 milliliter M-porosity sintered glass funnel, which was preheated to approximately 150°C with boiling DMF, and then washed thoroughly with three portions of 150 milliliters of boiling DMF, followed by washing with three portions of 150 milliliters of DMF at room temperature, and then three portions of 50 milliliters of methanol, thus providing 10.3 grams (72 percent yield) of a shiny purple pigment, which was identified as Type I TiOPc by XRPD.

#### **EXAMPLE II: Preparation of Type V Titanyl Phthalocyanine**

50 [0038] Fifty grams of TiOPc Type I were dissolved in 300 milliliters of a trifluoroacetic acid/methylene chloride (1/4, volume/volume) mixture for 1 hour in a 500-milliliter Erlenmeyer flask with magnetic stirrer. At the same time, 2600 milliliters of methanol/methylene chloride (1/1, volume/volume) quenching mixture was cooled with a dry ice bath for 1 hour in a 3000 milliliter beaker with magnetic stirrer, and the final temperature of the mixture was about -25°C. The TiOPc solution was transferred to a 500-milliliter addition funnel with a pressure-equalization arm, and added into the cold quenching mixture over a period of 30 minutes. The mixture was then allowed to stir for an additional 30 minutes. The mixture was hose-vacuum filtered through a 2000-milliliter Buchner funnel with fibrous glass frit of 4-8µm in porosity. The pigment was then well mixed with 1500 milliliters of methanol in the funnel, and vacuum filtered. The pigment was then well mixed with 1000 milliliters of hot water (>90°C), and vacuum filtered in the funnel for four times. The pigment was then well mixed with 1500 milliliters of cold water, and vacuum filtered in the funnel. The final water filtrate was

measured for conductivity, which was below  $10\mu\text{S}$ . The resulting wet cake contained approximately 50 weight percent of water. A small portion of the wet cake was dried at  $65^\circ\text{C}$  under vacuum and a blue pigment was obtained. A representative XRPD of the TiOPc obtained after quenching with methanol/methylene chloride is depicted in Figure 3. The XRPD of the TiOPc obtained after quenching in the methanol/methylene chloride mixture is designated as a Type Y titanyl phthalocyanine.

[0039] The remaining portion of the wet cake was re-dispersed in 700 grams of monochlorobenzene (MCB) in a 1000-milliliter bottle and rolled for an hour. The dispersion was vacuum filtered through a 2000-milliliter Buchner funnel with a fibrous glass frit of  $4\text{-}8\mu\text{m}$  in porosity over a period of two hours. The pigment was then well mixed with 1500 milliliters of methanol and filtered in the funnel for two times. The final pigment was vacuum dried at  $60\text{-}65^\circ\text{C}$  for two days. Approximately 45g of the pigment were obtained. A representative XRPD of the TiOPc after MCB conversion is depicted in Figure 4. The XRPD of the TiOPc after the MCB conversion is designated as a Type V titanyl phthalocyanine.

#### EXAMPLE III: Preparation of a Type V Titanyl Phthalocyanine

[0040] Fifty grams of TiOPc Type I was dissolved in 300 milliliters of a trifluoroacetic acid/methylene chloride (1/4, volume/volume) mixture for 1 hour in a 500-milliliter Erlenmeyer flask with magnetic stirrer. At the same time, 2600 milliliters of a methanol/methylene chloride (3/1, volume/volume) quenching mixture was cooled with a dry ice bath for 1 hour in a 3000 milliliter beaker with magnetic stirrer, and the final temperature of the mixture was about  $-10^\circ\text{C}$ . The TiOPc solution was transferred to a 500-milliliter addition funnel with a pressure-equalization arm, and added into the cold quenching mixture over a period of 60 minutes. The mixture was then allowed to stir for an additional 30 minutes. The mixture was hose-vacuum filtered through a 2000-milliliter Buchner funnel with a fibrous glass frit of  $4\text{-}8\mu\text{m}$  in porosity. The pigment was then well mixed with 1500 milliliters of methanol in the funnel and vacuum filtered. The pigment was then well mixed with 1000 milliliters of hot water ( $>90^\circ\text{C}$ ) and vacuum filtered in the funnel for four times. The pigment was then well mixed with 1500 milliliters of cold water and vacuum filtered in the funnel. The final water filtrate was measured for conductivity, which was below  $10\mu\text{S}$ . The resulting wet cake contained approximately 50 weight percent of water. The wet cake was re-dispersed in 700 grams of monochlorobenzene (MCB) in a 1 000-milliliter bottle and rolled for an hour. The dispersion was vacuum filtered through a 2000-milliliter Buchner funnel with fibrous glass frit of  $4\text{-}8\mu\text{m}$  in porosity over a period of two hours. The pigment was then well mixed with 1500 milliliters of methanol and filtered in the funnel for two times. The final pigment was vacuum dried at  $60\text{-}65^\circ\text{C}$  for two days. Approximately 45g of the pigment were obtained.

#### COMPARATIVE EXAMPLE I: Preparation of Type IV Titanyl Phthalocyanine

[0041] Five hundred grams of TiOPc Type I was dissolved in 5 liters of a 1/4 (volume/volume) mixture of trifluoroacetic acid and methylene chloride over a period of approximately 15 minutes. A 1/1 (v/v) methanol/water mixture (50 liters), which had been cooled overnight to about  $0^\circ\text{C}$ , was divided into three equal portions and placed in three plastic 5 gallon pails. The dissolved pigment solution was also divided into three equal portions and added dropwise to the chilled methanol/water over a period of 1 hour. The precipitated solid clung to the sides of the pails, allowing for removal of the solvents by simple decantation. The solid was then redispersed in methanol (50 liters), and filtered through a Buchner Funnel (600 centimeter diameter) fitted with a glass fiber filter paper, and then washed with approximately 50 liters of hot water ( $60\text{-}80^\circ\text{C}$ ). The wet cake was then re-dispersed in monochlorobenzene (50 liters) and filtered as before. The washed pigment was then oven dried at  $70^\circ\text{C}$  overnight to afford 455 grams (91% yield) of a powdery blue pigment, which was identified as Type IV titanyl phthalocyanine by XRPD (Figure 6).

[0042] Figure 4 provides a XRPD spectrum for a Type VTiOPc pigment prepared by a process according to the present disclosure, and Figure 5 provides a XRPD of the TiOPc pigment of Comparative Examples I. As shown in Figure 4, a Type V TiOPc prepared by a process according to the present disclosure has four characteristic peaks at  $9.0^\circ$ ,  $9.6^\circ$ ,  $24.0^\circ$ , and  $27.2^\circ$  and is distinguishable from the Type IV TiOPc pigments (Figure 5).

[0043] Figures 8-10 show TEM and SEM micrographs of a Type V TiOPc prepared by the process of Example II, and SEM micrograph of a Type IV TiOPc prepared according to Comparative Example I. The Type V TiOPc exhibited a surface area of about  $40\text{ m}^2/\text{g}$  as compared to  $20\text{ m}^2/\text{g}$  for the TiOPc of Comparative Example I.

[0044] The UV spectra of TiOPc dispersions were also examined. TiOPc dispersions were prepared comprising TiOPc pigments (10% solids in mill base) and a poly (vinyl butyral) BM-S polymeric binder in n-butyl acetate by milling the components for three hours using Attritor milling. The dispersions had a TiOPc/binder make up of 60/40 (weight/weight). Example V had a TiOPc made in accordance with Example II, Comparative Example II included a TiOPc made in accordance with Comparative Example I. The UV spectra of the dispersions are shown in FIGURE 9.

**Photoreceptor Devices**

[0045] Several photoreceptor devices were prepared to compare the various electrical properties of different photo-generating pigments in a photoreceptor. In general, the photoreceptor devices comprised an undercoat layer, a charge generating layer, and a charge transport layer. The specific details of the devices are described with reference to the specific examples.

[0046] The following properties were measured in the various studies as follows: Sensitivity (S) is measured as the initial slope of a photoinduced discharge characteristic (PIDC) curve (in units of (volt cm<sup>2</sup>/ergs)), and  $V_{\text{depl}}$  is linearly extrapolated from the surface potential versus charge density relation of the device and is a measurement of voltage leak during charging. Dark decay ( $V_{\text{dd}}$ ) is the lost potential before light exposure. In general, an ideal photoreceptor device should have higher sensitivity (S) while  $V_{\text{dd}}$  and  $V_{\text{depl}}$  should be close to zero.

[0047] All the devices were coated with a 3-component undercoat layer, varying TiOPc charge generating layer and 30 $\mu\text{m}$  charge transport layer, respectively. The 3-component undercoat layer was prepared as follows: Zirconium acetylacetonate tributoxide (35.5 parts),  $\gamma$ -aminopropyltriethoxysilane (4.8 parts) and poly(vinyl butyral) BM-S (2.5 parts) were dissolved in n-butanol (52.2 parts). The coating solution was coated via a ring coater, and the layer was pre-heated at 59°C for 13 minutes, humidified at 58°C (dew point=54°C) for 17 minutes, and then dried at 135°C for 8 minutes. The thickness of the undercoat layer was approximately 1.3 $\mu\text{m}$ . The TiOPc generating layer dispersions were prepared as described in the following examples, coated on top of 3-component undercoat layer. The thickness of the photogenerating layer was approximately 0.2 $\mu\text{m}$ . Subsequently, a 30 $\mu\text{m}$  charge transport layer (CTL) was coated on top of the photo-generating layer from a solution of N,N'-diphenyl-N,N-bis(3-methyl phenyl)-1,1'-biphenyl-4,4'-diamine (9.9 grams) and a polycarbonate, PCZ-400 [poly(4,4'-dihydroxy-diphenyl-1-1-cyclohexane,  $M_w=40000$ )] available from Mitsubishi Gas Chemical Co., Ltd. (12.1 grams), in a mixture of 55 grams of tetrahydrofuran (THF) and 23.5 grams of monochlorobenzene. The CTL was dried at 135 degrees Centigrade for 45 minutes.

**EXAMPLE IV: Preparation of TiOPc Type Y charge generating layer coating dispersion**

[0048] Three grams of TiOPc Type Y (the intermediate pigment of Example II), 2 grams of poly(vinyl butyral) (BM-S) and 45 grams of n-butyl acetate was Attritor milled with 150 grams of 1.0-1.25 mm Glen Mills glass beads for 2 hours. The resulting dispersion was filtered through a 20 $\mu\text{m}$  Nylon cloth filter, and diluted to 5 weight percent solid before coating.

**EXAMPLE V: Preparation of TiOPc Type V charge generating layer coating dispersion**

[0049] Three grams of TiOPc Type V (Example II), 2 grams of poly(vinyl butyral) (BM-S) and 45 grams of n-butyl acetate was Attritor milled with 150 grams of 1.0-1.25 mm Glen Mills glass beads for 2 hours. The resulting dispersion was filtered through a 20 $\mu\text{m}$  Nylon cloth filter, and diluted to 5 weight percent solid before coating.

**EXAMPLE VI: Preparation of TiOPc Type V charge generating layer coating dispersion**

[0050] Three grams of TiOPc Type V (Example III), 2 grams of poly(vinyl butyral) (BM-S) and 45 grams of n-butyl acetate was Attritor milled with 150 grams of 1.0-1.25 mm Glen Mills glass beads for 2 hours. The resulting dispersion was filtered through a 20 $\mu\text{m}$  Nylon cloth filter, and diluted to 5 weight percent solid before coating.

**EXAMPLE VII: Preparation of TiOPc Type V charge generating layer coating dispersion**

[0051] Three grams of TiOPc Type V (Example II), 2 grams of a vinyl chloride/vinyl acetate copolymer (VMCH) ( $M_n=27000$ , about 86 weight percent of vinyl chloride, about 13 weight percent of vinyl acetate and about 1 weight percent of maleic acid) available from Dow Chemical and 45 grams of n-butyl acetate was Attritor milled with 150 grams of 1.0-1.25 mm Glen Mills glass beads for 2 hours. The resulting dispersion was filtered through a 20 $\mu\text{m}$  Nylon cloth filter, and diluted to 5 weight percent solid before coating.

**COMPARATIVE EXAMPLE II: Preparation of TiOPc Type IV charge generating layer coating dispersion**

[0052] Three grams of TiOPc Type IV (Comparative Example I), 2 grams of poly(vinyl butyral) (BM-S) and 45 grams of n-butyl acetate was Attritor milled with 150 grams of 1.0-1.25 mm Glen Mills glass beads for 2 hours. The resulting dispersion was filtered through a 20 $\mu\text{m}$  Nylon cloth filter, and diluted to 5 weight percent solid before coating.

[0053] The electrical performance was evaluated, and photo-induced discharge curves (PIDC) were obtained with a scanner speed of 61 rpm and a 122ms delay after exposure with 780nm light. The results are set forth in Table 1.



Device	TiOPc charge generating layer	S (Vcm <sup>2</sup> /erg)	V <sub>depl</sub> (V)	V <sub>dd</sub> (V)
1	Example IV	-500	200	85
2	Example V	-615	20	10
3	Example VI	-605	25	15
4	Example VII	-625	30	17
5	Comparative Example II	-490	30	15

## Claims

1. A process for the preparation of a Type V titanyl phthalocyanine having an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta$  0.2° at about 9.0°, 9.6°, 24.0°, and 27.2°, the process comprising:

providing a Type I titanyl phthalocyanine;  
dissolving said Type I titanyl phthalocyanine in a solution comprising a trihaloacetic acid and an alkylene halide;  
adding said mixture comprising the dissolved Type I titanyl phthalocyanine to a solution comprising an alcohol and an alkylene halide thereby precipitating a Type Y titanyl phthalocyanine; and  
treating said Type Y titanyl phthalocyanine with monochlorobenzene to yield a Type V titanyl phthalocyanine.

2. The process according to claim 1, wherein said solution comprising an alcohol and an alkylene halide has an alcohol to alkylene halide ratio of from 1/4 (v/v) to 4/1 (v/v).

3. The process according to claim 1, wherein said solution comprising an alcohol and an alkylene halide has an alcohol to alkylene halide ratio of from 1/1 (v/v) to 3/1 (v/v).

4. The process according to claim 1, wherein said solution comprising an alcohol and an alkylene halide comprises methanol and methylene chloride.

5. The process according to claim 1, wherein said Type Y titanyl phthalocyanine is treated with monochlorobenzene over a period of from 1 to 24 hours to obtain the resultant Type V titanyl phthalocyanine.

6. A process for the preparation of Type V titanyl phthalocyanine having an x-ray diffraction pattern having characteristic diffraction peaks at a Bragg angle  $2\theta$  0.2° at about 9.0°, 9.6°, 24.0°, and 27.2°, the process comprising:

dissolving a Type I titanyl phthalocyanine in a solution of trifluoroacetic acid and methylene chloride;  
precipitating a Type Y titanyl phthalocyanine by adding said solution of trifluoroacetic acid, methylene chloride and the Type I titanyl phthalocyanine to a solution of methanol and methylene chloride;  
washing said Type Y titanyl phthalocyanine; and  
converting the Type Y titanyl phthalocyanine to a Type V titanyl phthalocyanine by treating said Type Y titanyl phthalocyanine with monochlorobenzene.

7. The process according to claim 6, wherein said solution of methanol and methylene chloride has a methanol to methylene chloride ratio (v/v) of from 1/4 to 4/1.

8. The process according to claim 6, wherein said solution of methanol and methylene chloride has a methanol to methylene chloride ration (v/v) of from 1/1 to 3/1.

## Patentansprüche

1. Verfahren zur Herstellung eines Typ V-Titanylphthalocyanins mit einem Röntgenbeugungsdiagramm mit charakteristischen Beugungspeaks bei einem Bragg-Winkel  $2\theta$  von 0,2° bei ungefähr 9,0°, 9,6°, 24,0° und 27,2°, wobei das Verfahren umfasst:

das Bereitstellen eines Typ I-Titanylphthalocyanins;  
 das Auflösen des Typ I-Titanylphthalocyanins in einer Lösung, die eine Trihalogenessigsäure und ein Alkyl-  
 halogenid umfasst;  
 das Zugeben der Mischung, die das gelöste Typ I-Titanylphthalocyanin umfasst, zu einer Lösung, die einen  
 Alkohol und ein Alkylhalogenid umfasst, wodurch ein Typ Y-Titanylphthalocyanin ausgefällt wird; und  
 das Behandeln des Typ Y-Titanylphthalocyanins mit Monochlorbenzol, um ein Typ V-Titanylphthalocyanin zu  
 erhalten.

2. Verfahren nach Anspruch 1, wobei die Lösung, die einen Alkohol und ein Alkylhalogenid umfasst, ein Alkohol-  
 zu-Alkylhalogenid-Verhältnis von 1/4 (Vol./Vol.) bis 4/1 (Vol./Vol.) aufweist.

3. Verfahren nach Anspruch 1, wobei die Lösung, die einen Alkohol und ein Alkylhalogenid umfasst, ein Alkohol-  
 zu-Alkylhalogenid-Verhältnis von 1/1 (Vol./Vol.) bis 3/1 (Vol./Vol.) aufweist.

4. Verfahren nach Anspruch 1, wobei die Lösung, die einen Alkohol und ein Alkylhalogenid umfasst, Methanol und  
 Methylenchlorid umfasst.

5. Verfahren nach Anspruch 1, wobei das Typ Y-Titanylphthalocyanin über einen Zeitraum von 1 bis 24 Stunden mit  
 Monochlorbenzol behandelt wird, um das resultierende Typ V-Titanylphthalocyanin zu erhalten.

6. Verfahren zur Herstellung von Typ V-Titanylphthalocyanin mit einem Röntgenbeugungsdiagramm mit charakteri-  
 stischen Beugungspeaks bei einem Bragg-Winkel  $2\theta$  von  $0,2^\circ$  bei ungefähr  $9,0^\circ$ ,  $9,6^\circ$ ,  $24,0^\circ$  und  $27,2^\circ$ , wobei das  
 Verfahren umfasst:

das Auflösen eines Typ I-Titanylphthalocyanins in einer Lösung von Trifluoressigsäure und Methylenchlorid;  
 das Ausfällen eines Typ Y-Titanylphthalocyanins durch Zugeben der Lösung von Trifluoressigsäure, Methylen-  
 chlorid und dem Typ I-Titanylphthalocyanin zu einer Lösung von Methanol und Methylenchlorid;  
 das Waschen des Typ Y-Titanylphthalocyanins; und  
 das Umwandeln des Typ Y-Titanylphthalocyanins in ein Typ V-Titanylphthalocyanin durch Behandeln des Typ  
 Y-Titanylphthalocyanins mit Monochlorbenzol.

7. Verfahren nach Anspruch 6, wobei die Lösung von Methanol und Methylenchlorid ein Methanol-zu-Methylenchlorid-  
 Verhältnis (Vol.Nol.) von 1/4 bis 4/1 aufweist.

8. Verfahren nach Anspruch 6, wobei die Lösung von Methanol und Methylenchlorid ein Methanol-zu-Methylenchlorid-  
 Verhältnis (Vol.Nol.) von 1/1 bis 3/1 aufweist.

## Revendications

1. Procédé pour la préparation d'une titanyl phtalocyanine de type V présentant un diagramme de diffraction des  
 rayons X ayant des pics de diffraction caractéristiques à un angle  $2\theta$  de Bragg de  $0,2^\circ$  à environ  $9,0^\circ$ ,  $9,6^\circ$ ,  $24,0^\circ$   
 et  $27,2^\circ$ , le procédé comprenant :

la fourniture d'une titanyl phtalocyanine de type I ;  
 la dissolution de ladite titanyl phtalocyanine de type I dans une solution comprenant un acide trihalogénoacétique  
 et un halogénure d'alkylène ;  
 l'ajout dudit mélange comprenant la titanyl phtalocyanine de type I dissoute à une solution comprenant un alcool  
 et un halogénure d'alkylène précipitant ainsi une titanyl phtalocyanine de type Y ; et  
 le traitement de ladite titanyl phtalocyanine de type Y par du monochlorobenzène pour donner une titanyl  
 phtalocyanine de type V.

2. Procédé selon la revendication 1, dans lequel ladite solution comprenant un alcool et un halogénure d'alkylène a  
 un rapport de l'alcool sur l'halogénure d'alkylène de 1/4 (v/v) à 4/1 (v/v).

3. Procédé selon la revendication 1 dans lequel ladite solution comprenant un alcool et un halogénure d'alkylène a  
 un rapport de l'alcool sur l'halogénure d'alkylène de 1/1 (v/v) à 3/1 (v/v).

## EP 1 672 034 B1

4. Procédé selon la revendication 1, dans lequel ladite solution comprenant un alcool et un halogénure d'alkylène comprend du méthanol et du chlorure de méthylène.

5 5. Procédé selon la revendication 1, dans lequel ladite titanyl phtalocyanine de type Y est traitée par du monochlorobenzène sur une période de 1 à 24 heures pour obtenir la titanyl phtalocyanine de type V résultante.

10 6. Procédé pour la préparation d'une titanyl phtalocyanine de type V présentant un diagramme de diffraction des rayons X ayant des pics de diffraction caractéristiques à un angle  $2\theta$  de Bragg de  $0,2^\circ$  à environ  $9,0^\circ$ ,  $9,6^\circ$ ,  $24,0^\circ$  et  $27,2^\circ$ , le procédé comprenant :

la dissolution d'une titanyl phtalocyanine de type I dans une solution d'acide trifluoroacétique et de chlorure de méthylène ;

15 la précipitation d'une titanyl phtalocyanine de type Y par l'ajout de ladite solution d'acide trifluoroacétique, de chlorure de méthylène et de titanyl phtalocyanine de type I à une solution de méthanol et de chlorure de méthylène ;

le lavage de ladite titanyl phtalocyanine de type Y ; et

la conversion de la titanyl phtalocyanine de type Y en une titanyl phtalocyanine de type V par le traitement de ladite titanyl phtalocyanine de type Y avec du monochlorobenzène.

20 7. Procédé selon la revendication 6, dans lequel ladite solution de méthanol et de chlorure de méthylène a un rapport du méthanol sur le chlorure de méthylène (v/v) de 1/4 à 4/1.

25 8. Procédé selon la revendication 6, dans lequel ladite solution de méthanol et de chlorure de méthylène a un rapport du méthanol sur le chlorure de méthylène (v/v) de 1/1 à 3/1.

30

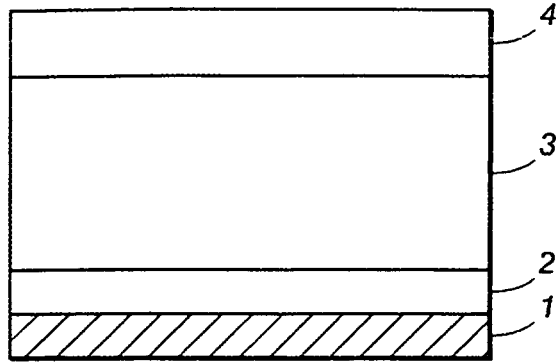
35

40

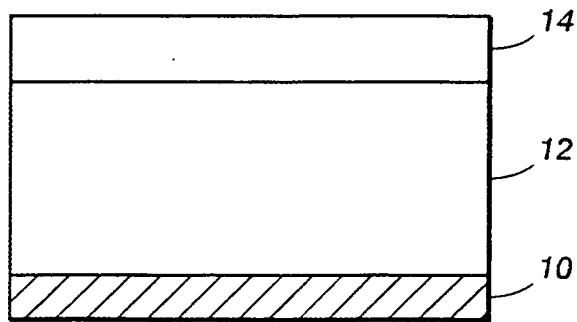
45

50

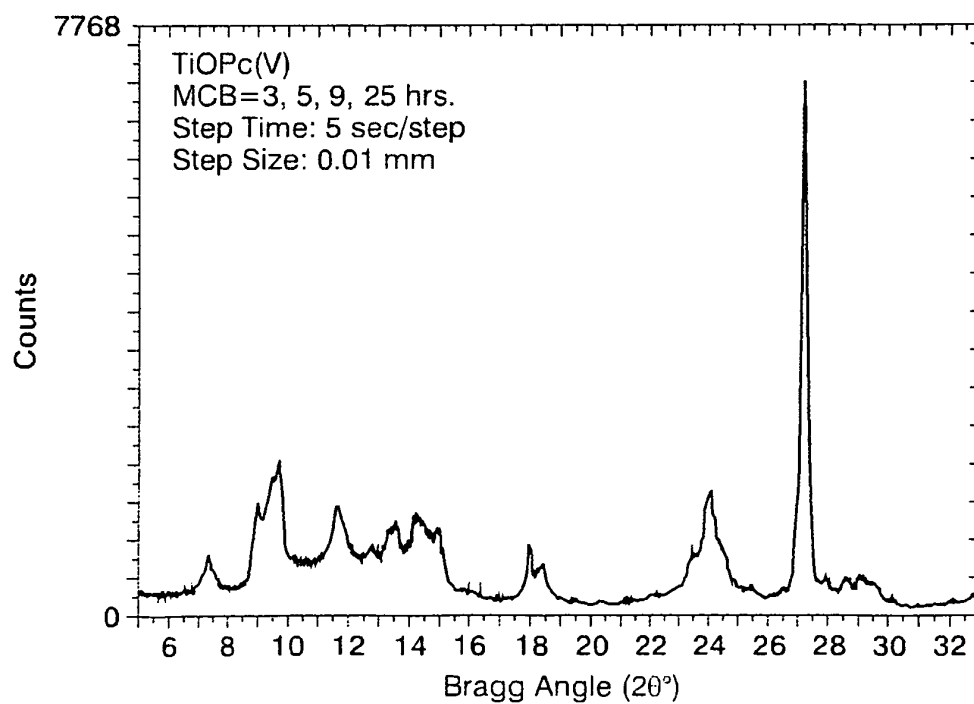
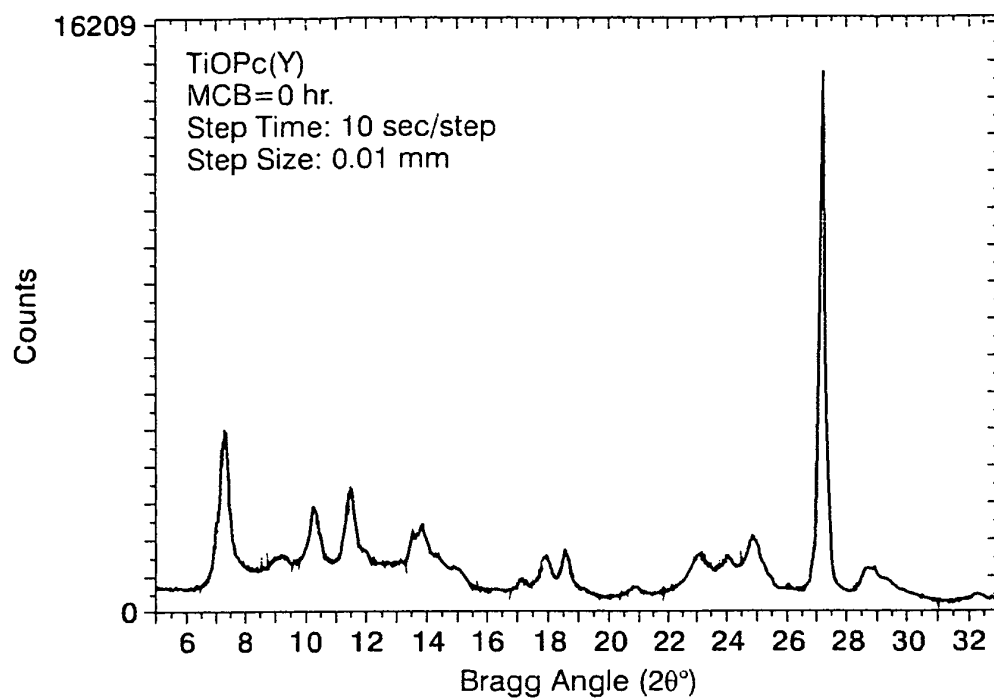
55



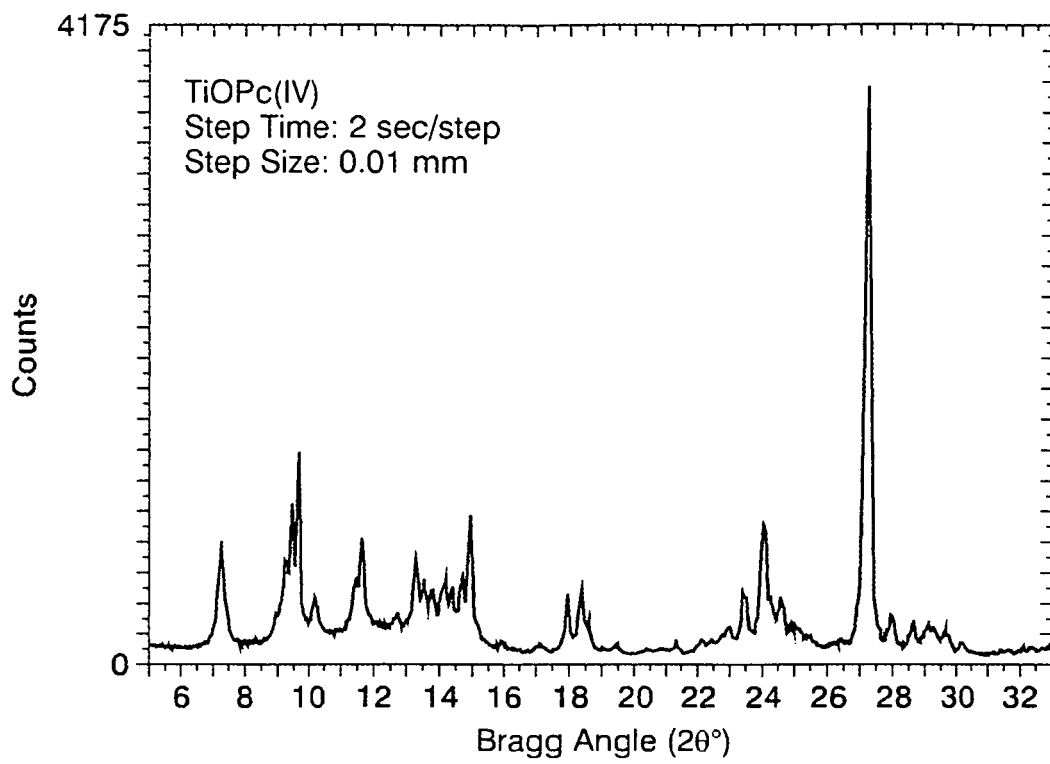
**FIG. 1**

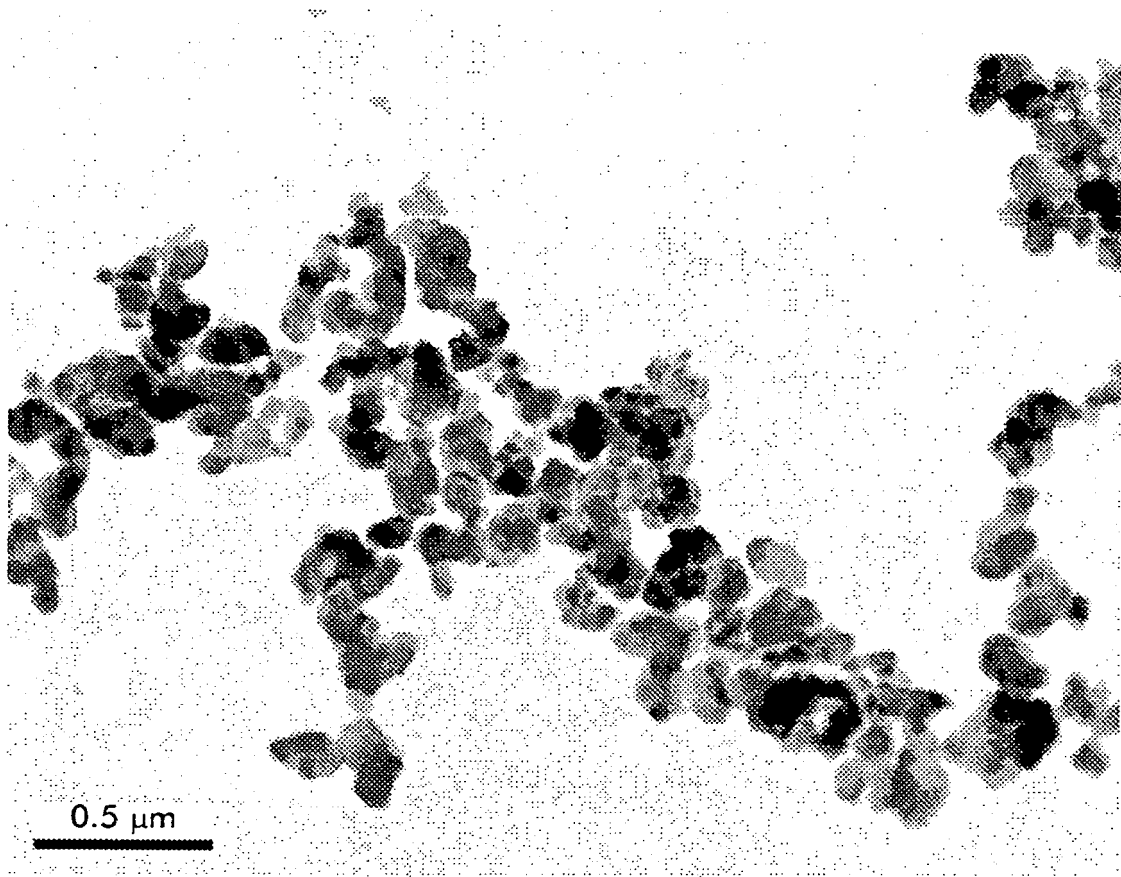


**FIG. 2**

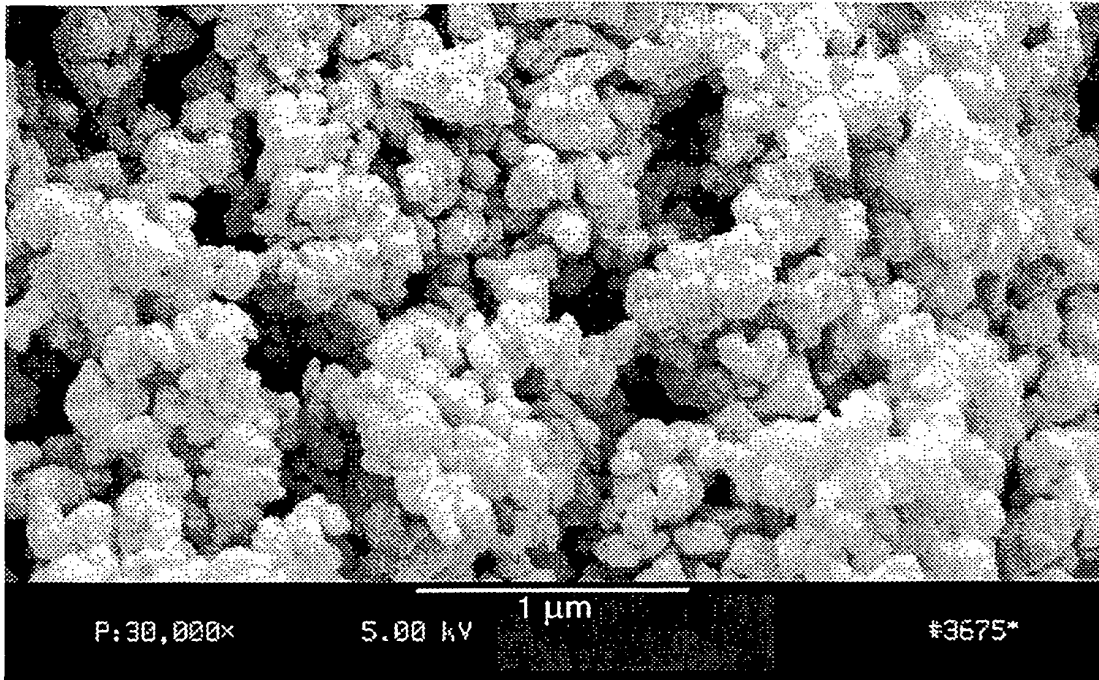
**FIG. 3****FIG. 4**

**FIG. 5**

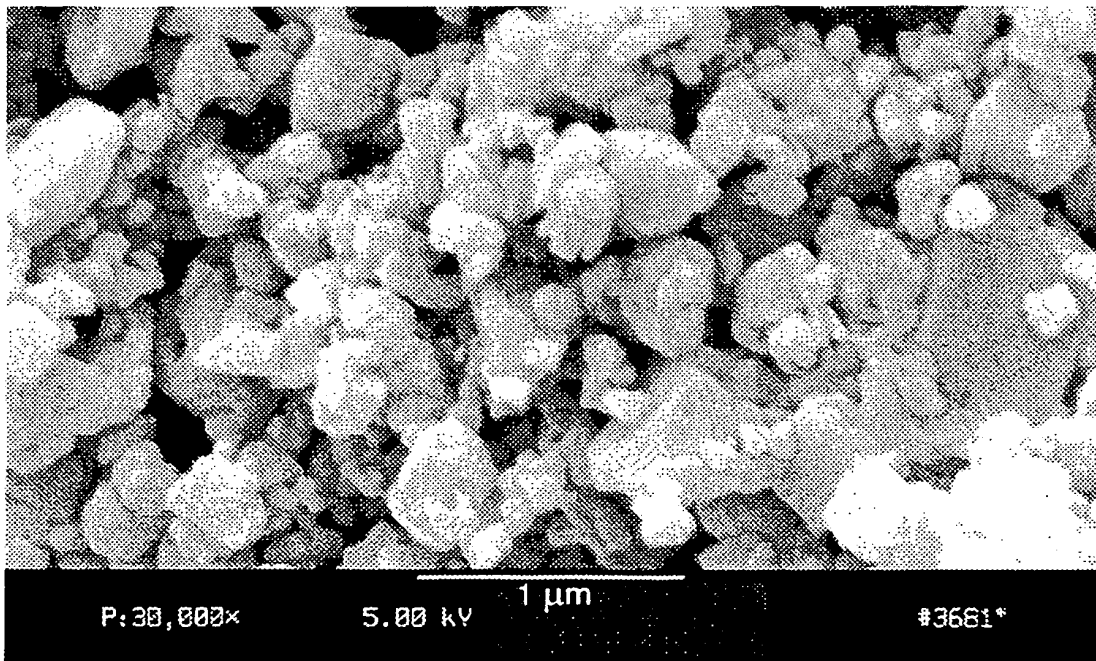




**FIG. 6**

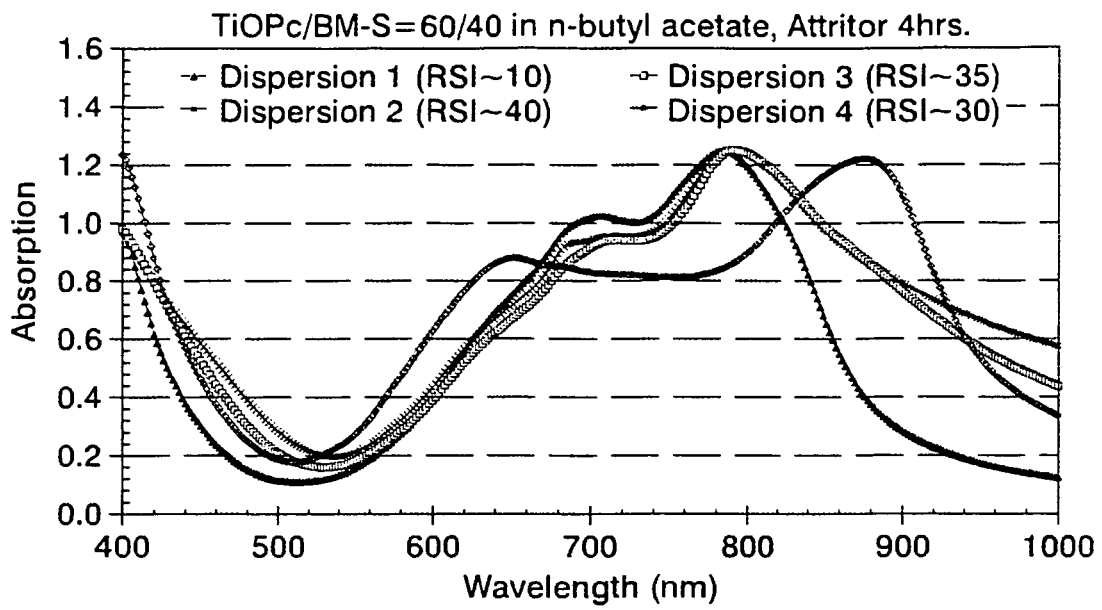


**FIG. 7**



**FIG. 8**





**FIG. 9**

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- US 4265990 A [0003]
- US 5189155 A [0011] [0024]
- US 5189156 A [0011] [0024]
- US 5153094 A [0011] [0024]
- US 5166339 A [0011] [0024]
- WO 9945074 A [0013]
- EP 0482922 A [0014]
- EP 0409737 A [0015]
- EP 0810267 A [0016]
- EP 0560311 A [0017]